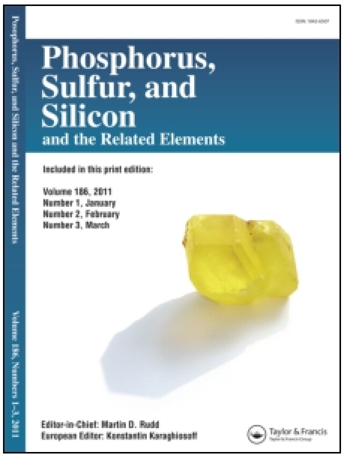

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Transition Metal Complexes of Dis(thiosemicarbazone): Synthesis and Spectral, and Antifungal Studies

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To cite this Article Refat, Moamen S. , Chandra, Sulekh and Tyagi, Monika(2010) 'Transition Metal Complexes of Dis(thiosemicarbazone): Synthesis and Spectral, and Antifungal Studies', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 1, 22 — 33

To link to this Article: DOI: 10.1080/10426500802713234

URL: http://dx.doi.org/10.1080/10426500802713234

Phosphorus, Sulfur, and Silicon, 185:22–33, 2010
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802713234

TRANSITION METAL COMPLEXES OF DIS(THIOSEMICARBAZONE): SYNTHESIS AND SPECTRAL, AND ANTIFUNGAL STUDIES

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Mn(II), Co(II), Ni(II), and Cu(II) complexes have been synthesized with benzil bis(thiosemicarbazone) (L) and characterized by elemental analyses, molar conductance measurements, magnetic susceptibility measurements, thermogravimetric studies, infrared (IR), electronic, and electron paramagnetic resonance (eEPR) spectral studies. The molar conductance measurements of the complexes in DMF correspond to the non-electrolytic nature of the complexes. Thus these complexes may be formulated as $[M(L)X_2]$ (where M = Mn(II), Co(II), Ni(II), Cu(II) and X = Cl^- and NO_3^-). On the basis of IR, electronic, and EPR spectral studies, an octahedral geometry has been assigned for Mn(II), Co(II), and Ni(II) complexes, whereas a tetragonal geometry for the Cu(II) complexes is presumed. The free ligand and its metal complexes were tested against the phytopathogenic fungi (i.e., **Rhizoctonia baticola, Alternaria alternata*****) in vitro.***

INTRODUCTION

Thiosemicarbazones and their metal complexes have considerable interest for researchers because of their biological activities such as antitumor, antiviral, anticancer, antifungal, antibacterial, and antimalarial properties.[1–10] They also have been used as drugs, and are reported to possess a wide variety of biological activities against bacteria, fungi, and certain types of tumors, and they also serve as a useful model for bioinorganic processes.[11] They have been studied extensively due to their flexibility, their selectivity and sensitivity towards the central metal atom, their structural similarities with natural biological substances, and also due to the presence of an imine group (-N=CH-) that imparts biological activity.[12]

Bis(thiosemicarbazones) form copper complexes, which show a broad spectrum of biological activity and so are of great pharmacological interest.[13,14] They have been investigated for various uses including as anticancer chemotherapeutic agents[15] and as superoxide

Received 23 September 2008; accepted 22 December 2008.

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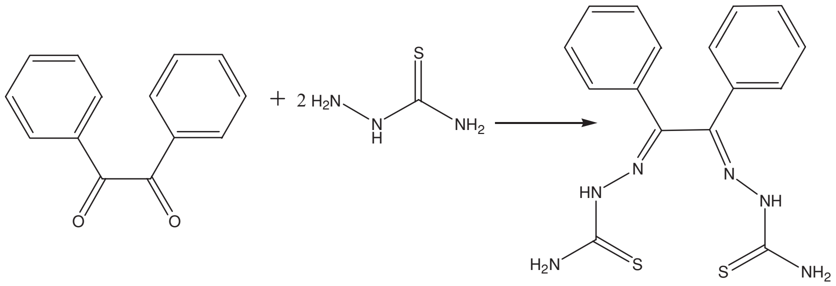


Figure 1 Synthesis and structure of the ligand.

dismutase-like radical scavengers.[16] It is, however, the hypoxia selectivity of certain copper bis(thiosemicarbazones) and their use as delivery agents for radioactive copper in the development of new copper-based radiopharmaceuticals that has created much recent interest.[17,18] Copper plays a crucial role in several enzymes that catalyze oxidation/reduction reactions related to an antioxidant system of the organism.[19] This metal ion has also been found in many metalloproteins.[20] It takes part in a variety of processes in living organisms, such development of embryos, formation of tissues, control of body temperature, and nerve cell functions.[21] Because of their biological activity and analytical application, thiosemicarbazides and thiosemicarbazones, as well as their metal complexes, have been the subject of many studies.[22,23]

In the present article, we report the synthesis, and spectral and biological studies of Mn(II), Co(II), Ni(II), and Cu(II) complexes with benzil bis(thiosemicarbazone) (L). The structure of the ligand is shown in Figure 1.

The complexes were synthesized by reacting the ligand with the metal ions in a 1:1 molar ratio in ethanolic medium. The molar conductance of the complexes in DMF lies in the range 8–15 $\Omega^{-1}cm^2mol^{-1}$ indicating their non-electrolytic behavior.[24] Thus the complexes may be formulated as $[M(L)X_2]$ (where M = Mn(II), Co(II), Ni(II), and Cu(II); L = benzil bis(thiosemicarbazone) and X = Cl^-, NO_3^-).

EXPERIMENTAL

All the chemicals used were of Analar grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received.

Physical Measurements

The C, H, and N were analyzed on Carlo-Erba 1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as a calibrant. Diamagnetic corrections were made by using Pascal's constants. Electronic impact mass spectrum was recorded on Jeol, JMS-DX-303 mass spectrometer. IR spectra (KBr) were recorded on FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. Thermogravimetric analysis (TGA and DTG) were carried out in a dynamic nitrogen atmosphere (30 mL/min) with a heating rate of 10°C/min using a Shimadzu TGA-50H thermal analyzer. EPR spectra of the Mn(II) and Cu(II) complexes were recorded as polycrystalline sample at room temperature E_{4-} on an EPR spectrometer using the DPPH as the g-marker. The molecular weights of complexes were determined cryoscopically in benzene.

Synthesis of the Ligand (L)

The benzil bis(thiosemicarbazone) ligand was prepared using published procedures.[25] A hot ethanolic solution (20 mL) of thiosemicarbazide (1.82 g, 0.02 mol) and an ethanolic solution (25 mL) of benzil (2.1g, 0.01 mol) were mixed in the presence of few drops of conc. HCl with constant stirring. This mixture was refluxed at 60–70°C for 3 h. The completion of the reaction was confirmed by TLC. The reaction mass was degassed on a rotary evaporator over a water bath. The degassed reaction mass upon cooling gave cream colored crystals. It was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}. Yield (65%), mp 164°C. Elemental analysis of the complexes is existed in Table I. The electronic impact mass spectrum of the ligand, which shows a molecular ion (M^+) peak at m/z = 357 amu corresponding to the species $[C_{16}H_{16}N_4S_2]^+$, confirms the proposed formula.

Synthesis of Complexes

A hot ethanolic solution (20 mL) of the corresponding metal salts (0.01 mol) was mixed with a hot ethanolic solution of the respective ligand (0.01 mol). The mixture was heated under reflux for 3–4 h at 50–60°C. Upon cooling the contents, the colored complex was separated out in each case. It was filtered and washed with 50% ethanol and dried under vacuum over P_4O_{10}. The purity of the complexes was checked by thin layer chromatography (TLC). TLC analysis was performed on silica gel (Fluka F_{60} 254 20 × 20; 0.2 mm) using the solvent system n-heptane/acetone (2:1) as eluent.

RESULTS AND DISCUSSION

IR Spectra

In the IR spectrum of ligand, the ν(N-H) band appeared at 3237 cm^{-1}, which indicates that in the solid state, the ligand remains as the thione tautomer. The position of the ν(C=N) band of the thiosemicarbazone appeared at 1608 cm^{-1} and is shifted towards a lower wave number in the complexes, indicating coordination via the azomethane nitrogen.[26,27] This is also confirmed by the appearance of bands in the range 459–489 cm^{-1}; this has been assigned to the ν(M-N). A strong band found at 1106 cm^{-1} is due to the ν(N-N) group of the thiosemicarbazone. The position of this band is shifted towards a higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethane nitrogen. The band appearing at *ca.* 837 cm^{-1} ν(C=S) in the IR spectrum of ligand is shifted towards a lower wave number. It indicates that the thione sulfur coordinates to the metal ion.[28] Thus, it may be concluded that the ligand behaves as a tetradentate chelating agent coordinating through azomethane nitrogen and thiolate sulfur. The presence of bands at 1412–1454, 1320–1342, and 1008–1078 cm^{-1} in the IR spectra of the metal complexes suggests that both the nitrate groups are coordinated to the central metal ion in a unidentate fashion.[29]

Table I Molar conductance and elemental analysis data of the complexes

Complexes	Color	Molar cond. $\Omega^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$	Yield (%)	Mp (°C)	Elemental analysis found (calculated) (%)			
					M	C	H	N
$[Mn(L)Cl_2]$ $MnC_{16}H_{16}N_6S_2Cl_2$	Brown	10	65	275	11.38(11.41)	39.79(39.83)	3.35(3.32)	17.46(17.43)
$[Mn(L)(NO_3)_2]$ $MnC_{16}H_{16}N_8S_2O_6$	Brown	12	60	279	10.32(10.28)	35.81(35.89)	2.93(2.99)	20.87(20.93)
$[Co(L)Cl_2]$ $CoC_{16}H_{16}N_6S_2Cl_2$	Rust orange	25	62	259	12.16(12.12)	39.47(39.50)	3.24(3.29)	17.25(17.28)
$[Co(L)(NO_3)_2]$ $CoC_{16}H_{16}N_8S_2O_6$	Rust red	18	60	263	10.89(10.92)	35.56(35.62)	2.93(2.96)	20.84(20.78)
$[Ni(L)Cl_2]$ $NiC_{16}H_{16}N_6S_2Cl_2$	Green	20	66	282	12.10(12.08)	39.48(39.50)	3.26(3.29)	17.29(17.28)
$[Ni(L)(NO_3)_2]$ $NiC_{16}H_{16}N_8S_2O_6$	Light green	8	70	290	10.85(10.89)	35.64(35.62)	2.98(2.96)	20.75(20.78)
$[Cu(L)Cl_2]$ $CuC_{16}H_{16}N_6S_2Cl_2$	Green	14	72	176	12.92(12.93)	39.08(39.10)	3.24(3.26)	17.14(17.11)
$[Cu(L)(NO_3)_2]$ $CuC_{16}H_{16}N_8S_2O_6$	Green	9	66	180	11.62(11.67)	35.26(35.29)	2.90(2.94)	20.55(20.59)

Table II Magnetic moment and electronic spectra of the complexes

Complexes	$\mu_{eff.}$ (BM)	$\lambda_{max}(cm^{-1})$
$[Mn(L)Cl_2]$	5.95	18248, 24509, 28570, 34482
$[Mn(L)(NO_3)_2]$	5.99	18868, 24631, 28985, 31055
$[Co(L)Cl_2]$	4.96	11086, 14715, 18416
$[Co(L)(NO_3)_2]$	4.87	11198, 15385, 18621
$[Ni(L)Cl_2]$	2.89	9337, 14124, 24096
$[Ni(L)(NO_3)_2]$	2.95	9671, 14388, 24570
$[Cu(L)Cl_2]$	1.95	15432, 25575, 33670
$[Cu(L)(NO_3)_2]$	1.92	15290, 25380, 32570

Magnetic Moments and Electronic Spectra

The Mn(II) complexes show a magnetic moment recorded at room temperature in the 5.95–5.99 BM range (Table II), corresponding to high spin with five unpaired electrons. The electronic spectra of Mn(II) complexes exhibit four weak intensity absorption bands in the range 18248–18868, 24509–24631, 28570–28985, and 31055–34482. These bands may be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ (^4G) (10B+5C), and $^6A_{1g} \rightarrow {}^4E_g$ (^4D) (17B+5C), respectively. The fourth band may be assigned to charge transfer.[30]

At room temperature, the Co(II) complexes show a magnetic moment in the range 4.87–4.96 BM corresponding to three unpaired electrons. The electronic spectra of Co(II) complexes, recorded in DMSO solution, exhibit absorption ion the region, 11096–11198, 14715–15385, and 18416–18621 cm^{-1}. These bands may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) transitions, respectively.[31]

The Ni(II) complexes show a magnetic moment recorded at room temperature in the 2.89–2.95 BM range, corresponding to two unpaired electrons. The electronic spectra of the Ni(II) complexes display three absorption bands in the range 9337–9671, 14124–14388, and 25380–25575 cm^{-1}. These bands may be assigned to three spin allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}$ (F) (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (F) (ν_2), and $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P) (ν_3), respectively.[32]

At room temperature, Cu(II) complexes show magnetic moment in the range 1.92–1.95 BM corresponding to one unpaired electron. The electronic spectra of Cu(II) complexes exhibit bands in the range 15290–15432 and 25380–25575cm^{-1}.[33] These bands correspond to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}(d_{x2\text{-}y2} \rightarrow d_{z2})\nu_1$ and $^2B_{1g} \rightarrow {}^2B_{2g}(d_{x2\text{-}y2} \rightarrow d_{zy})\nu_2$, respectively.

EPR Spectra

The EPR spectra of Mn(II) complexes were recorded at room temperature as polycrystalline samples and in DMSO solution (Table III). The polycrystalline spectra gave an isotropic signal centered at approximately the free electron g—value (go = 2.0023). The broadening of the spectra is probably due to spin relaxation. In DMSO solution the complexes give six well resolved lines due to hyperfine interaction between the unpaired electrons with the Mn nucleus (I = 5/2).

The EPR spectra of Co(II) complexes were recorded as polycrystalline sample and in DMSO solutions at liquid nitrogen temperature. The g values were found to be almost same in both cases. This indicates that the complexes have same geometry in solid form as well as in the solution.

Table III EPR spectral data of the complexes

		Data as polycrystalline sample			Data as DMSO sample		
Complexes	Temp.	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A°/g_{iso}
$[Mn(L)Cl_2]$	RT	—	—	2.17	—	—	166.7
$[Mn(L)(NO_3)_2]$	RT	—	—	2.07	—	—	122.6
$[Co(L)Cl_2]$	LNT	2.20	1.92	2.02	2.25	1.98	2.07
$[Co(L)(NO_3)_2]$	LNT	2.22	1.88	2.00	2.24	2.04	2.10
$[Cu(L)Cl_2]$	RT	2.10	2.03	2.05	2.16	2.02	2.06
$[Cu(L)(NO_3)_2]$	RT	2.25	2.12	1.16	2.20	2.07	2.11

Room temperature EPR spectra of Cu(II) complexes were recorded as polycrystalline sample, on X band at frequency 9.1 GHz under the magnetic field strength 3000 G. The analysis of spectra gave $g_{\parallel} = 2.10–2.25$, $g_{\perp} = 2.03–2.14$. The observed $g_{|}$ values for the complexes are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{\parallel} > g_{|} > 2.0023$ observed for the complexes indicates that unpaired electron is localized in the d_{x2-y2} orbital of the Cu(II) ion, and the spectral features are characteristic of axial symmetry.[34]

Ligand Field Parameters

Various ligand field parameters were calculated for the complexes and are listed in Table IV. The values of D_q in Co(II) complexes were calculated from transition energy ratio diagram using the ν_3/ν_2 ratio. The Nehelauxetic parameter β was readily obtained by using the relation $\beta = B$ (free ion)/B (complex), where B (free ion) for Mn(II) is 786 cm^{-1}, for Co(II) is 1120 cm^{-1}.[35,36] Our results are in agreement with the complexes reported earlier.[37,38] The values of β lie in the range 0.58–0.78. These values β and hx indicate the appreciable covalent character of the metal–ligand σ bond. In the Mn(II), the values B and C were calculated from the second and third transitions, because these transitions are free from the crystal field splitting and depend on B and C parameters.[37] Slater Condon–Shortly parameter F_2 and F_4 are related to the Racah parameter B and C as: $B = F_2 - 5F_4$ and $C = 35F_4$.

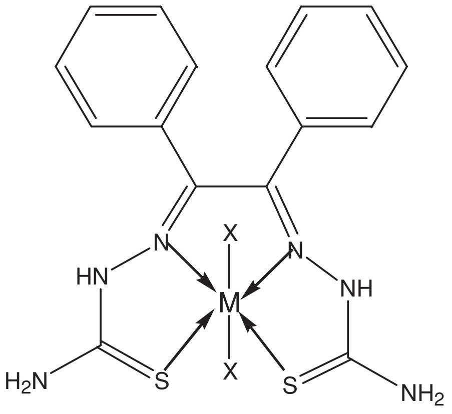
On the basis of above spectral studies, the structures in Figure 2 may be suggested for the complexes.

Thermogravimetric Analysis

Thermal analysis diagrams (TG/DTG) of the studies complexes are represented in Figure 3.

Table IV Ligand field parameters of the complexes

Complexes	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	β	F_4	F_2	h_x	LFSE (kj/mol)
$[Mn(L)Cl_2]$	1824	580	3741	0.73	106.88	1114.40	3.85	—
$[Mn(L)(NO_3)_2]$	1886	622	3682	0.79	105.20	1148.00	3.00	—
$[Co(L)Cl_2]$	1385.74	770	—	0.69	—	—	—	133
$[Co(L)(NO_3)_2]$	1399.74	778	—	0.69	—	—	—	134
$[Ni(L)Cl_2]$	934	681	—	0.66	—	—	—	134
$[Ni(L)(NO_3)_2]$	967	663	—	0.63	—	—	—	139



[M= Mn(II), Co(II), Ni(II) ,Cu(II) and X=Cl$^-$, NO$_3^-$,]

Figure 2 Suggested structure of the complexes.

The bis(thiosemicarbazone) ligand melts at 437 K with simultaneous decomposition (Figure 3A). The first mass loss was observed at 603 K. From the TG curve, it appears that the sample decomposes in only one stage over the temperature range 393–1073 K. The mass loss was as follows: obs. = 71.81%, calc. = 73.03%.

The thermal decomposition of Cu(II), Co(II), Ni(II), and Mn(II) bis(thiosemicarbazone) complexes occurs at two main steps. The first degradation step take place in the range of 393–598 K, and it corresponds to the degradation of two amino groups and coordinated anions ($2NO_3^-$ or $2Cl^-$). Table V lists the decomposition steps dealing with the loss of the remaining organic sample. The metal carbide is the final residual at the end of the decomposition processes in all complexes.

Kinetic Studies

In recent years, there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves.[39–45] The most commonly used methods are the differential method of Freeman and Carroll,[39] integral method of Coats and Redfern,[40] and the approximation method of Horowitz and Metzger.[43]

In the present investigation, the general thermal behaviors of the bis(thiosemicarbazone) complexes, in terms of stability ranges, peak temperatures, and values of kinetic parameters, are shown in Table VI. The kinetic parameters have been evaluated using the Coats–Redfern equation:

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^{n}} = \frac{A}{\varphi} \int_{T_1}^{T_2} \exp\left(-\frac{E^*}{RT}\right) dt \tag{1}$$

This equation upon integration gives

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right] \tag{2}$$

A plot of the left-hand side (LHS) against *1/T* was drawn. E^* is the energy of activation in J mol^{-1} and calculated from the slope and A in (s^{-1}) from the intercept value. The entropy of activation ΔS^* in (JK^{-1}mol^{-1}) was calculated by using the equation

$$\Delta S^* = R\ln(Ah/k_B T_S) \tag{3}$$

where k_B is the Boltzmann constant, h is the Plank's constant, and T_s is the DTG peak temperature.[46]

The entropy of activation, ΔS^*, was calculated from Equation 3. The enthalpy activation, ΔH^*, and Gibbs free energy, ΔG^*, were calculated from $\Delta H^* = E^* - RT$ and $\Delta G^* = \Delta H^* - T\Delta S^*$, respectively.

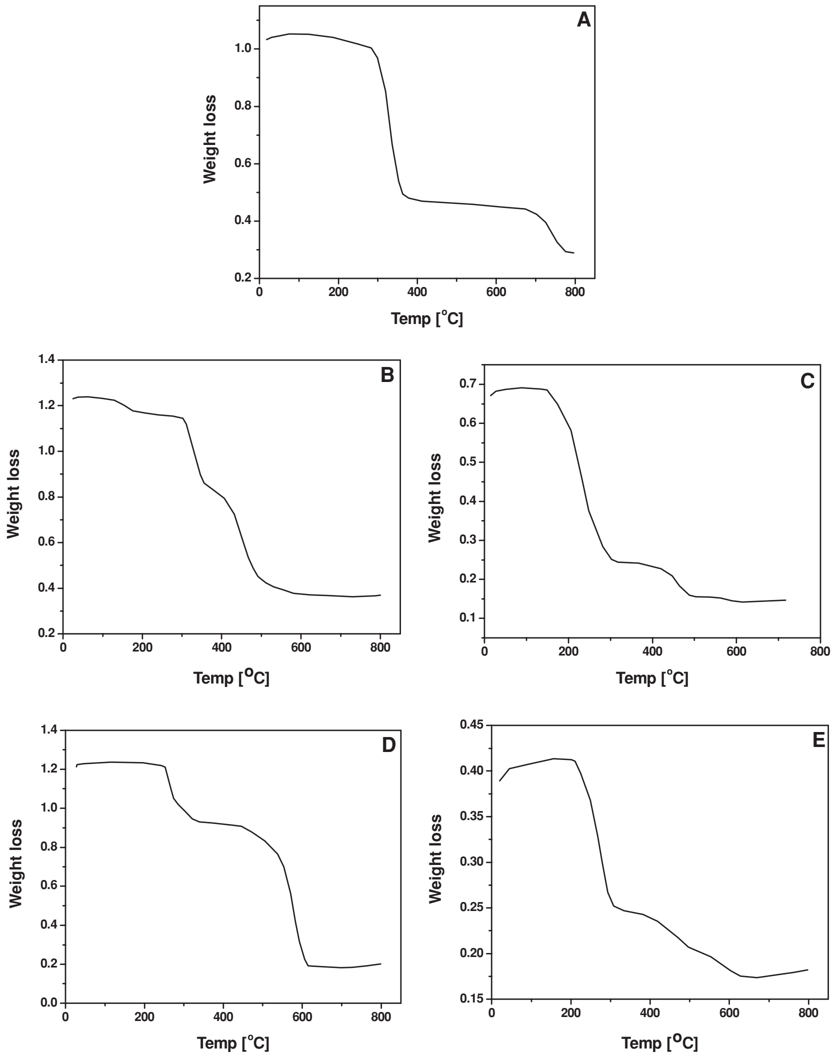


Figure 3 TG curves of (A): ligand, (B): $CuCl_2/L$, (C): $Cu(NO_3)_2/L$, (D): $CoCl_2/L$ (E): $Co(NO_3)_2/L$, (F): $NiCl_2/L$, (G): $Ni(NO_3)_2/L$, (H): $MnCl_2/L$, and (I): $Mn(NO_3)_2/L$. *(Continued)*

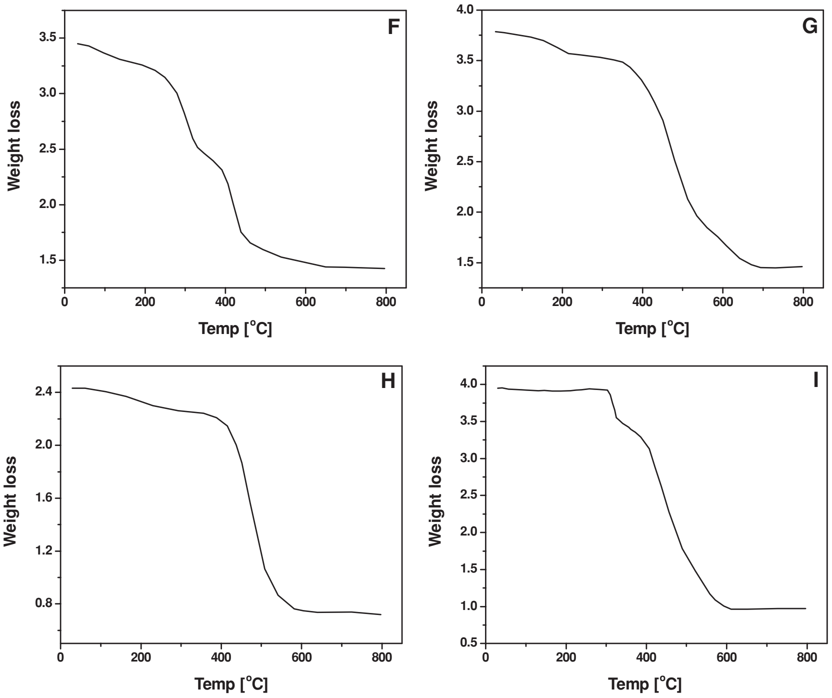


Figure 3 (Continued)

Table V Thermal data of the bis(thiosemicarbazones) and their complexes

				TG Weight loss (%)		
Compound	Steps	Temperature range (°C)	DTG peak (°C)	Calc.	Found	Assignments of loss moieties
Ligand (L)	1st	120–800	330	73.03	71.81	$C_8H_{16}N_6S_2$
$CuCl_2$/L	1st	125–250	183	69.93	70.09	$[C_9H_{16}N_6S_2Cl_2]$
	2nd	250–800	450			
$Cu(NO_3)_2$/L	1st	120–200	180	79.48	78.48	$[C_{12}H_{16}N_8S_2O_6]$
	2nd	200–800	435			
$CoCl_2$/L	1st	170–290	260	82.94	83.88	$[C_{14}H_{16}N_6S_2Cl_2]$
	2nd	290–800	550			
$Co(NO_3)_2$/L	1st	183–281	265	53.44	53.48	$[H_{16}N_8S_2O_6]$
	2nd	281–800	560			
$NiCl_2$/L	1st	156–310	280	58.27	58.64	$[C_4H_{16}N_6S_2Cl_2]$
	2nd	310–800	420			
$Ni(NO_3)_2$/L	1st	160–325	285	62.38	61.54	$[C_4H_{16}N_8S_2O_6]$
	2nd	325–800	450			
$MnCl_2$/L	1st	130–300	275	71.18	70.63	$[C_9H_{16}N_6S_2Cl_2]$
	2nd	300–800	510			
$Mn(NO_3)_2$/L	1st	147–300	270	76.28	75.42	$[C_{10}H_{16}N_8S_2O_6]$
	2nd	300–800	564			

Table VI Kinetic parameters using the coats–redfern (CR) equation for transition metal complexes of cis(thiosemicarbazone)

	Parameter					
Compounds	E (J mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (J mol^{-1})	ΔG (J mol$^{-1)}$	r
Ligand (L)	4.22×10^4	3.21×10^3	-2.79×10^2	6.55×10^5	5.99×10^5	0.9790
$CuCl_2$/L	2.56×10^5	2.34×10^9	3.75×10	6.11×10^5	5.94×10^5	0.9795
$Cu(NO_3)_2$/L	3.11×10^5	3.18×10^{10}	-2.18×10	3.44×10^5	3.57×10^5	0.9980
$CoCl_2$/L	3.21×10^5	5.87×10^7	-2.41×10^2	5.14×10^5	4.73×10^5	0.9812
$Co(NO_3)_2$/L	3.46×10^5	8.35×10^{12}	-5.11×10^2	3.98×10^5	3.73×10^5	0.9892
$NiCl_2$/L	5.49×10^5	7.23×10^8	-3.90×10^2	4.19×10^5	4.34×10^5	0.9983
$Ni(NO_3)_2$/L	5.61×10^5	7.54×10^7	-1.98×10^2	3.33×10^5	3.73×10^5	0.9992
$MnCl_2$/L	7.95×10^5	8.11×10^5	2.77×10^2	2.59×10^5	2.49×10^5	0.9862
$Mn(NO_3)_2$/L	8.84×10^5	2.20×10^{10}	4.11×10^2	3.38×10^5	3.34×10^5	0.9943

ΔG is positive for the reaction for which ΔH is positive and ΔS is negative. The reaction for which ΔG is positive and ΔS is negative considered as unfavorable or as a nonspontaneous reaction.

Reactions are classified as either exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$) on the basis of whether they give off or absorb heat. Reactions can also be classified as exergonic ($\Delta G < 0$) or endergonic ($\Delta G > 0$) on the basis of whether the free energy of the system decreases or increases during the reaction.

The activation energy of Mn^{+2} complexes is expected to increase in relation with decrease in their radii.[47] The smaller size of the ions permits a closer approach of the ligand. Hence, the *E* value in the first stage for the Mn^{+2} complexes is higher than that for the other Cu^{+2} complex.

The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9790 to 0.9992, showing a good fit with a linear function. It is clear that the thermal decomposition process of all bis(thiosemicarbazone) complexes is nonspontaneous, i.e., the complexes are thermally stable.

Antifungal Studies

The preliminary fungitoxicity screening of the compounds at different concentrations was performed in vitro against the test fungi, *R. bataticola* and *A. alternata*, by the food poison technique.[48] Stock solutions of compounds were prepared by dissolving the compounds in DMF. Chlorothalonil was used as commercial fungicide and DMF served as control. Potato dextrose agar medium was prepared by using potato, dextrose, agar-agar, and distilled water. Appropriate quantities of the compounds in DMF were added to potato dextrose agar medium in order to obtain concentrations of 250 and 125 ppm of compound in the medium. The medium was poured into a set of two Petri plates under aseptic conditions in a laminar flow hood. When the medium in the plates was solidified, a mycelial disc of 0.5 cm in diameter cut from the periphery of the 7 days old culture, and it was aseptically inoculated upside down in the center of the Petri plates. These treated Petri plates were incubated at $26 \pm 1°C$ until fungal growth in the control Petri plates was almost complete.

The inhibition of fungal growths expressed in percentage terms was determined on the growth in test plates compared to the respective control plates as given inhibition%:

inhibition% = 100 (C−T)/C (where C, diameter of the fungal growth on the control, T; diameter of the fungal growth on the test plate). All the compounds show fungal growth inhibition in the following order Cu(II) > Ni(II) > Co(II) > Mn(II) ≅ligand.

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